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Non-additivity of multiply charged ion emission from Si and Al produced by molecular projectiles

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Abstract

Experiments are reported on the non-additivity of a multiply charged ion emission with various atomic and molecular projectiles. A distinction has been found in the non-additivity of the Si^{2+} emission from Si. It manifests itself as a change of the non-additivity factor $K_{2,1}$ from $K_{2,1} < 1$ (sub-linear effect) to $K_{2,1} > 1$ (non-additive enhancement effect) in going from Au_2^- to Cu_2^- projectiles. It was shown that the sub-linear behaviour of $K_{2,1}$ is caused by the correlated move of projectiles gold atoms in a target matter (the clearing-the-way effect) and the origin of the non-additive enhancement is not determined by non-linear cascade sputtering. On the basis of the results obtained a new effect in an ion-induced atomic-like Auger electron emission has been predicted.

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1. Introduction

It is known that a singly charged ion (SCI) emission from solids bombarded by keV atomic ions results mainly from linear cascade sputtering [1]. As compared with atomic ions, molecular ions produce a higher energy density in the impact region due to spatial localization ($\sim 10^{-15}$ cm^2) and temporal synchronization ($<10^{-14}$ s) of the constituent atom collisions with the surface. According to a non-linear cascade concept [2], a molecular ion impact initiates the development of non-linear cascades, which are responsible for non-additive sputtering of solids as various neutral and charged species [3]. The non-additivity factor $K_{m,1}$ a measure of non-additive sputtering, is described as

$$K_{m,1} = Y_m / mY_1, \qquad (1)$$

where Y_m and Y_1 are the yields of species of interest sputtered by m-atomic and atomic projectiles with the same velocity. For SCIs sputtered from metals and Si by keV/atom diatomic projectiles, typical $K_{2,1}$ values are $K_{2,1} > 1$ [4,5]. Experiments [6] and Molecular Dynamics (MD) simulations [7] have

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shown that non-additive sputtering increases the sputtered flux owing to low energy atomic species ejected as a result of low energetic collisions at the later stage of a cascade evolution.

By now the mechanism of a multiply charged ion (MCI) emission from Si and Al bombarded by keV atomic projectiles seems to be well understood. In the kinetic model [8], the MCI creation is interpreted as a three-step process which involves with (i) the ejection of the singly or doubly ionized atoms with the 2p-vacancy to the vacuum, (ii) the partial neutralization of such species near the surface by electron tunnelling and (iii) the Auger decay of surviving 2p-vacancies beyond an electron tunnelling range, generating both MCI and atomic-like LMM or L^2MM Auger electron emissions. According to the molecular orbital (MO) model [9], the 2p-vacancy ions are created during a collision between two atoms. In this case, a transient molecule is formed and if the inter-nuclear distance is smaller than a critical value R_{th} then some MOs can overlap each other, causing a promotion of one or two core electrons of the lighter colliding partner into high-lying empty levels. Singly 2p-vacancy ions are created in both asymmetric and symmetric collisions while doubly 2p-vacancy ions result only from asymmetric collisions [10,11]. The threshold energy E_{th} of the electron promotion collisions increases with decreasing R_{th}. For asymmetric collision between the heavier projectile and a lighter target atom, the threshold energy $E_{th,a}$ is higher than that $E_{th,s}$ for symmetric collision between two target atoms. Experiments [10,11] and MD simulations [12] evidence that, under the bombardment of Si and Al by atomic projectiles with the energy $E_0 > E_{th,a}$, the 2p-vacancy ions are ejected mainly from the surface as a result of asymmetric energetic collisions at the earliest stage of a collision cascade evolution.

The use of the MCI emission as a probe, gives a unique possibility to study molecular projectile-solid interactions in a very short time scale ($\sim 10^{-14}$ s) at the moment when non-linear cascades have not yet developed. Such a study can show the role of energetic collisions in non-additive sputtering, which is of a fundamental interest in physics of both inelastic collisions in solids and the ionization process in sputtering.

For the first time, the non-additivity of the MCI emission has been studied in [5]. Under the bombardment of silicon by 9 keV/atom Au_m^- projectiles ($m = 1,\ 2$), a sub-linear effect with $K_{2,1} = 0.62$ ($K_{2,1} < 1$) was discovered. A sub-linear effect manifests itself as a decrease of the Si^{2+} yield per atom Y_m/m with increasing number of atoms in the projectile m from 1 to 2. In recent work [13] this unexpected result was re-examined and confirmed for the same projectile-target system and $K_{2,1} = 0.76$ was obtained.

At the present work the question is addressed of the origin of sub-linear effect in MCI emission. For this purpose, a study of both MCI and SCI emissions produced from the Si and Al targets by Au_m^- and Cu_m^- projectiles with energies of several keV/atom was carried out.

2. Experimental

Two experimental setups were used. The first one uses a secondary ion mass spectrometer equipped with a sputter Au_m^- ion source [14], which was described earlier [4,5]. Au_m^- ions ($m = 1$–3) with energies of $E_0 = 9$ and 18 keV and current densities of $j \sim 10^{-7}$ A/cm^2 bombarded the Si surface at an incidence angle of 45°. The Si surface was cleaned by Au_m^- ions bombardment and heating up to a temperature of 1400 K. A surface cleanliness was monitored by detecting the SiO ions and its yield dropped by two orders of magnitude after the cleaning procedure. The surface prepared in such a way was believed to be a "clean". During the measurements, the target temperature was 1400 K and the residual pressure $P \leqslant 1.10^{-5}$ Pa.

The second setup uses a Cameca IMS 4f instrument. The Cu_m^- ion source, similar to the previous one [14], was mounted on the instrument and replaced the duoplasmatron source. Cu_m^- ions ($m = 1$–4) with energies of $E_0 = 6.8$ and 13.6 keV bombarded the Si and Al targets. The Cu_m^- ion currents measured with the primary Faraday cup of the instrument were of the order of 0.2–2 nA. The Cu_m^- beams were focused on the sample surface to a spot size of a 60 μm. The raster-scanned area was of 150 μm^2. The Si and Al samples with stated purity of 99.99% were used. The targets were cleaned by Cu^- bombardment during one hour. During the measurements, the targets were at the room temperature and $P \leqslant 1.10^{-6}$ Pa. To avoid an ambiguity due to interference of singly charged ions at the same mass-to-charge ratio, MCI emission from Si was measured for the isotope ^{29}Si.

3. Results and discussion

In our experiments, MCI and SCI emissions were studied for the following "projectile-target" systems: 13.6 keV Cu_m^- ($m = 1$–3) on Si; 6.8 keV Cu_m^- ($m = 1$–4) on Si; 13.6 keV Cu_2^- on Al; 6.8 keV Cu_m^- ($m = 1$–3) on Al and 6.8 keV $Cu_3O_2^-$ on Al. The results related to the 18 keV Au_m^- ($m = 1$–3) on Si and 9 keV Au_m^- ($m = 1$–3) on Si systems were given from [5]. The values of $K_{2,1}$ were calculated from the secondary ion yields normalized to unit projectile current, using Eq. (1).

The $K_{2,1}$ values for the MCI and SCI emissions, presented in Table 1, demonstrate clearly the following features.

(1) For the Si^{2+} emission produced from Si by Au_m^- (9 keV/atom) projectiles ($m = 1, 2$), $K_{2,1}$ is equal to $K_{2,1} = 0.62$. Thus, the Au_2^- bombardment causes a reduction of the Si^{2+} yield per atom Y_m/m, leading to a sub-linear effect ($K_{2,1} < 1$).
(2) On the contrary, the bombardment of Si and Al by Cu_m^- (6.8 keV/atom) projectiles ($m = 1, 2$) leads to non-additive enhancement in the Si^{2+} and Al^{2+} ion yields Y_m/m ($K_{2,1} > 1$) with $K_{2,1} = 2.85$ and $K_{2,1} = 4.14$, respectively. For the Si^{3+} and Al^{3+} emissions the values of $K_{2,1}$ are equal to $K_{2,1} = 1.13$ and $K_{2,1} = 1.66$.
(3) In all studied cases, for the SCI emission, $K_{2,1} > 1$ and the value of $K_{2,1}$ is increased with increasing number of atoms in a sputtered particle n.

Table 1
The values of the non-additivity factor $K_{2,1}$ for the multiply charged ion (MCI) and singly charged ion (SCI) emissions for the following "projectile-target" systems: 9 keV/atom Au_m^- ($m = 1$–2) on Si and 6.8 keV/atom Cu_m^- ($m = 1$–2) on Si and Al

Projectile	Target	Emitted species	Non-additivity factor $K_{2,1}$
9 keV/atom Au_m^- ($m = 1, 2$)	Si	Si^{2+}	0.62
		Si^+	3.26
		Si_2^+	5.32
		Si_3^+	14.5
6.8 keV/atom Cu_m^- ($m = 1, 2$)	Si	Si^{3+}	1.13
		Si^{2+}	2.82
		Si^+	3.45
		Si_2^+	4.14
		Si_3^+	6.05
	Al	Al^{3+}	1.66
		Al^{2+}	4.14
		Al^+	3.25
		Al_2^+	6.89
		Al_3^+	8.72

Thus, as compared with the SCI emission (for which $K_{2,1} > 1$ always), the Si^{2+} emission from Si produced by Au_2^- and Cu_2^- projectiles demonstrates a change of $K_{2,1}$ from $K_{2,1} < 1$ (sub-linear effect) to $K_{2,1} > 1$ (non-additive enhancement effect). This indicates that the non-additivity is determined by a competition of, as a minimum, two processes and, in this case, $K_{2,1}$ can be represented as $K_{2,1} = K_1K_2$ where $K_1 \leqslant 1$ and $K_2 \geqslant 1$ are the factors which are responsible for a decrease and a increase of the MCI emission. Probably, one of these processes, which is responsible for a decrease of the MCI yield, dominates under the bombardment of Si by Au_2^- projectiles so that a sub-linear effect ($K_{2,1} < 1$) manifests itself.

Amongst all studied cases, the Si^{2+} and Al^{2+} emissions were not found for the 9 keV Au_3^- on Si, 6.8 keV Cu_4^- on Si, and 6.8 keV $Cu_3O_2^-$ on Al. The Si^{3+} emission was not found for the 13.6 keV Cu_3^- on Si. The absence of the Si^{2+} emission for molecular 9 keV Au_3 and 6.8 keV Cu_4^- projectiles and its observation for atomic 9 keV Au^- and 6.8 keV Cu^- projectiles allows of the following conclusions.

(1) The three-body collisions between a diatomic projectile and a target atom do not play a visible role in the 2p-vacancy ion production.
(2) A 2p-vacancy ion creation originates from binary collisions between projectile atom-target atom or target atom-target atom and depends

on the projectile atom energy E_0/m rather than on the projectile energy E_0.

(3) A 2p-vacancy ion production caused by molecular ions obeys the projectile atom energy threshold E_{th}. For Au_3 and Cu_4^- ions, the values of E_{th} can be estimated roughly as $E_{th} \geqslant 3$ keV/atom and $E_{th} \geqslant 1.7$ keV/atom.

These values of E_{th} were used for an estimation of the threshold energy $E_{th,s}$ in symmetric collisions, assuming that the maximum energy $E_{th,s} = 4M_pM_t(M_p + M_t)^{-2}E_{th}$ can be transferred from the projectile to the target atom in the head-on collision (M_p and M_t are the masses of the projectile and target atoms). For Au^- (3 keV) on Si and Cu^- (1.7 keV) on Si collisions, the values of $E_{th,s}$ are equal $E_{th,s} = 1.3$ keV and $E_{th,s} = 1.4$ keV, respectively. They coincide with each other to 10% and agree with the values of $E_{th,s}$ for the Si–Si collisions determined in [10]. This evidences that the symmetric collisions are responsible for the Si^{2+} emission in the near threshold energy range. However, for $E_0 > E_{th,a}$, asymmetric collisions start playing the dominant role in the MCI creation [11]. This is confirmed by the appearance of the Si^{3+} emission at $E_0 > E_{th,a}$ ($E_{th,a} \geqslant 4.53$ keV/atom) that result only from asymmetric collisions.

The bombardment of Si by molecular ions can lead to a reduction of the 2p-vacancy ion production due to the mechanism of the clearing-the-way effect [15] that removes some atoms from the molecular projectile track in binary collisions between the front running projectile atom and the target atoms. As a result, the back running projectile atom(s) interact(s) with the target atom(s) at larger impact parameters and, in this case, the 2p-vacancy ion production will be smaller. Thus, during the molecular bombardment, the 2p-vacancy ion production averaged per constituent atom of projectile will be less than that for the atomic bombardment. The 2p-vacancy ion production must decrease with (i) increasing projectile atom mass M_p, with (ii) decreasing critical distance R_{th}, with (iii) decreasing of the energy E_0/m and with (iv) increasing of the number m of atoms in a projectile. These predictions were used, as a test, for the examinations of the clearing-the-way effect concept. The results of such examinations show a qualitative agreement with predictions.

(1) The decrease of M_p diminishes the role of the clearing-the-way effect in the MCI emission and $K_{2,1}$ is increased from $K_{2,1} < 1$ to $K_{2,1} > 1$ in moving from the Au_m^- projectiles to the Cu_m^- ones ($M_{Cu} < M_{Au}$), see Table 1. This fact allows us to predict the larger non-additive enhancement in the MCI emission under the bombardment of light element targets by light molecular projectiles.

(2) The comparison of $K_{2,1}$ for Si^{3+} and Si^{2+} ions and for Al^{3+} and Al^{2+} ions shows that $K_{2,1}$ (Si^{3+}) < $K_{2,1}$ (Si^{2+}) and $K_{2,1}$ (Al^{3+}) < $K_{2,1}$ (Al^{2+}).

(3) For Si^{2+} ions, the dependence of $K_{3,1}$ and $K_{2,1}$ on E_0/m shows (see Fig. 1) that the $K_{2,1}$ and $K_{3,1}$ values are increased with increasing of E_0/m from 4 to 9 keV/atom and, for a given value of E_0/m, $K_{2,1} > K_{3,1}$. These data were recalculated from results obtained under the bombardment of Si by the keV/atom Au_m^- projectiles in Fig. 7 of [13].

All these results allow us to conclude that, during the bombardment of Si by Au_2^- ions, the correlated move of projectile atoms in a target

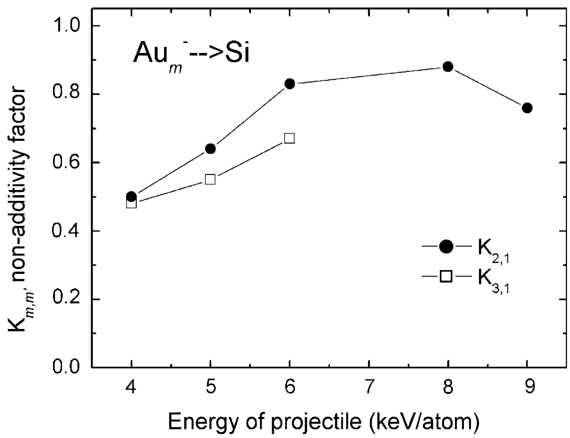

Fig. 1. The dependence of $K_{3,1}$ and $K_{2,1}$ on E_0/m. These data were recalculated from the results obtained under the bombardment of Si by the keV/atom Au_m^- projectiles (see Fig. 7 in [13]).

matter (the clearing-the-way effect) is the dominant process responsible for both the reduction of the 2p-vacancy ion creation (the first step of the Si^{2+} emission) and, as a final result, a sub-linear effect ($K_{2,1} < 1$). The SCIs result from collisions with the larger impact parameters at the later stage of a cascade evolution and, in this case, the reduction of the SCI emission due to the clearing-the-way effect must be negligible. The bombardment of metals and Si by Au_2^- projectiles leads to the non-additive enhancement of the SCI emission ($K_{2,1} > 1$) [4,5] which is defined by a joint action of two factors: non-additive sputtering of atoms caused by non-linear cascades and non-additive process of their charge formation [16].

In this context, a surprising result of our work is the discovery of the non-additive enhancement ($K_{2,1} > 1$) in the MCI emission which, as compared with the SCI emission, cannot be explained by non-linear cascade sputtering because of the MCI emission originates mainly from asymmetric collisions that occur at the earliest stage of the collision cascade evolution (the first 10–15 fs after the projectile impact [12]) when non-linear cascades have not yet developed.

The physical origin of the non-additive enhancement of the MCI emission cannot be identified at the present time. One possible explanation involves with the difference of the electron subsystem excitations (the appearance of non-occupied levels below the Fermi level) produced by the atomic and molecular projectiles in an impact region [17]. These electron excitations can decrease a neutralization probability of ejected 2p-vacancy atoms (the second step of the Si^{2+} emission) due to the resonant electron transfer from these atoms into non-occupied levels of the metal. However, this interpretation needs for an additional experimental basis.

Interestingly, up to now sub-linear effects ($K_{m,1} < 1$) were observed only in the electronic stopping related phenomena [18], for example, in a secondary ion-induced electron emission from solids. The results of this work allow us to predict a new effect in an ion-induced atomic-like Auger electron emission. Indeed, for the ion-induced atomic-like Auger electron emission, the dependence of $K_{2,1}$ on parameters of the "projectile-target" system must repeat that for the MCI emission because of both the multiply charged ion and the atomic-like Auger electron are created in the same event from the Auger decay of the 2p-vacancy atom beyond the surface. Thus, as opposed to a secondary electron emission from solids (for which the non-additivity factor $K_{2,1} < 1$ always), the ion-induced atomic-like Auger electron emission from silicon must demonstrate a change of $K_{2,1}$ from $K_{2,1} < 1$ to $K_{2,1} > 1$ in going from the Au_m^- to Cu_m^- projectiles.

4. Conclusion

The multiply charged ion emission from the Si and Al targets with various molecular projectiles has been studied. It has been found that, as compared with a singly charged (atomic and cluster) ion emission (on which the typical non-additivity factors $K_{2,1}$ are $K_{2,1} > 1$), the Si^{2+} emission from Si demonstrates a change of $K_{2,1}$ from $K_{2,1} < 1$ (sub-linear effect) to $K_{2,1} > 1$ (non-additive enhancement effect) in going from $Au_m{}^-$ to Cu_m^- projectiles. It was shown that a sub-linear effect is caused by the correlated move of projectiles gold atoms in a silicon target (the clearing-the-way effect). The origin of the non-additive enhancement in the Si^{2+} emission is not determined by non-linear cascade sputtering. On the basis of the results obtained a new effect in the ion-induced atomic-like Auger electron emission has been predicted.

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